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 (54) Title: NON-AQUEOUS COATING COMPOSITION BASED ON AN OXIDATIVELY DRYING ALKYD RESIN AND A PHOTO-INITIATOR (57) Abstract Proposed is a non-aqueous coating composition based on an oxidatively drying alkyd resin and a photo-initiator, where an acid or latent acid and one or more compounds of the group of vinyl ethers, acetals, and alkoxysilanes which are reactive in the presence of an acid are incorporated into the coating composition, said vinyl ethers, acetals, and alkoxysilanes preferably being covalently bonded to the alkyd resin. The ratio of the number of oxidatively drying groups present in the alkyd resin to the number of groups reactive in the presence of an acid preferably is in the range of 1/10 to 15/1. The acid preferably is the phosphoric acid dibutyl ester.			

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NON-AQUEOUS COATING COMPOSITION BASED ON AN
OXIDATIVELY DRYING ALKYD RESIN AND A PHOTO-INITIATOR

5 The invention pertains to a non-aqueous coating composition based on an oxidatively drying alkyd resin and a photo-initiator.

Such a coating composition has been proposed before in EP-A-234 641. The composition described in said document comprises an oxidatively 10 drying alkyd resin of comparatively low-molecular weight and an allyl ether group covalently bonded thereto, a siccative such as a cobalt salt and/or zirconium salt and, optionally, a photo-initiator. A drawback to the coating compositions described in said document is that curing at temperatures of 10°C or lower, in particular of thick coats, is not 15 satisfactory. A further drawback to the known coating compositions is that on curing acrolein is released.

The invention now provides a coating composition which can be cured without any problems also at low temperatures even after it has been 20 applied as a somewhat thicker coat.

The invention consists in that an acid or latent acid and one or more compounds belonging to the group of vinyl ethers, acetals, and alkoxysilanes which are reactive in the presence of an acid are 25 incorporated into a coating composition of the known type mentioned in the opening paragraph.

It should be noted that EP-A-234 641 mentions in passing the possibility to modify the employed alkyd resins with compounds preferably having at 30 least two reactive groups, such as polyisocyanates or polyalkoxysilanes. However, the reactivity of these groups is intended for their reaction with

the functional groups present in the alkyd resin during the preparation of the resin.

At least part of the alkyd resin composition optionally comprising several alkyd resins in the non-aqueous coating compositions according to the invention is oxidatively drying as a result of incorporating a large number of unsaturated, aliphatic compounds, at least a portion of which is poly-unsaturated. The unsaturated aliphatic compounds preferably are unsaturated aliphatic monocarboxylic acids, more particularly poly-unsaturated aliphatic monocarboxylic acids. Examples of mono-unsaturated fatty acids are myristoleic acid, palmitoleic acid, oleic acid, gadoleic acid, erucic acid, and ricinoleic acid. Preferably use is made of fatty acids containing conjugated double bonds, such as dehydrated ricinus oil fatty acid and/or wood oil fatty acid. Other monocarboxylic acids suitable for use include tetrahydrobenzoic acid and hydrogenated or non-hydrogenated abietic acid or its isomer. If so desired, the monocarboxylic acids in question may be used wholly or in part as triglyceride, e.g., as vegetable oil, in the preparation of the alkyd resin. If so desired, mixtures of two or more of such monocarboxylic acids or triglycerides may be employed, optionally in the presence of one or more saturated, (cyclo)aliphatic or aromatic monocarboxylic acids, e.g., pivalic acid, 2-ethylhexanoic acid, lauric acid, palmitic acid, stearic acid, 4-tert.butylbenzoic acid, cyclopentane carboxylic acid, naphthenic acid, cyclohexane carboxylic acid, 2,4-dimethyl benzoic acid, 2-methyl benzoic acid, and benzoic acid.

25

If so desired, also polycarboxylic acids may be incorporated into the alkyd resin, such as phthalic acid, isophthalic acid, terephthalic acid, 5-tert. butyl isophthalic acid, trimellitic acid, pyromellitic acid, succinic acid, adipic acid, 2,2,4-trimethyl adipic acid, azelaic acid, sebacic acid, dimerised fatty acids,

cyclopentane-1,2-dicarboxylic acid, cyclohexane-1,2-dicarboxylic acid, 4-methylcyclohexane-1,2-dicarboxylic acid, tetrahydrophthalic acid, endo-methylene-cyclohexane-1,2-dicarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, endoisopropylidene-cyclohexane-1,2-dicarboxylic acid,

5 cyclohexane-1,2,4,5-tetracarboxylic acid, and butane-1,2,3,4-tetracarboxylic acid. If so desired, the carboxylic acids in question may be used as anhydrides or in the form of an ester, e.g., an ester of an alcohol having 1-4 carbon atoms.

10 In addition, the alkyd resin can be composed of di- or polyvalent hydroxyl compounds. Examples of suitable divalent hydroxyl compounds are ethylene glycol, 1,3-propane diol, 1,6-hexane diol, 1,12-dodecane diol, 3-methyl-1,5-pentane diol, 2,2,4-trimethyl-1,6-hexane diol, 2,2-dimethyl-1,3-propane diol, and 2-methyl-2-cyclohexyl-1,3-propane diol. Examples of

15 suitable triols are glycerol, trimethylol ethane, and trimethylol propane. Suitable polyols having more than 3 hydroxyl groups are pentaerythritol, sorbitol, and etherification products of the compounds in question, such as ditrimethylol propane and di-, tri-, and tetrapentaerythritol. Preferably, use is made of compounds having 3-12 carbon atoms, e.g., glycerol,

20 pentaerythritol and/or dipentaerythritol.

The alkyd resins can be obtained by direct esterification of the constituent components, with the option of a portion of these components having been converted already into ester diols or polyester diols. Alternatively, the

25 unsaturated fatty acids can be added in the form of a drying oil, such as linseed oil, tuna fish oil, dehydrated castor oil, coconut oil, and dehydrated coconut oil. Transesterification with the other added acids and diols will then give the final alkyd resin. This transesterification generally takes place at a temperature in the range of 115 to 250°C, optionally with solvents such

as toluene and/or xylene also present. The reaction generally is carried out in the presence of a catalytic amount of a transesterification catalyst. Examples of transesterification catalysts suitable for use include acids such as p-toluene sulphonic acid, a basic compound such as an amine, or

5 compounds such as calcium oxide, zinc oxide, tetraisopropyl orthotitanate, dibutyl tin oxide, and triphenyl benzyl phosphonium chloride.

The number average molecular weight of the alkyd resin thus prepared preferably is at least 1000 and not more than 2800; favourable results can also be achieved at higher molecular weights, but this will be at the

10 expense of the solids content in the final coating composition.

The vinyl ether, acetal and/or alkoxy silane compounds used according to the invention preferably contain at least two vinyl ether, acetal and/or alkoxy silane groups and have a molecular weight of 150 or higher. Since

15 most commercially available vinyl ether, acetal and/or alkoxy silane compounds contain only one vinyl ether, acetal and/or alkoxy silane group and in addition at most one functional amino, epoxy, thiol, isocyanate, acrylic, hydride or hydroxyl group, first an adduct is formed of such a compound to a compound having at least two groups capable of reacting

20 with an amino, epoxy, thiol, isocyanate, acrylic, hydride or hydroxyl group. As examples may be mentioned compounds having an epoxy, isocyanate, hydroxyl and/or ester group or compounds with an ethylenically or ethynically unsaturated group incorporated therein.

25 Examples of at least difunctional, solid or liquid epoxy compounds suitable for use in the adduct in question include the di- or polyglycidyl ethers of (cyclo)aliphatic or aromatic hydroxy compounds such as ethylene glycol, glycerol, cyclohexane diol, mononuclear di- or polyvalent phenols, bisphenols such as Bisphenol-A and Bisphenol-F, and polynuclear phenols;

glycidyl ethers of fatty acids having, say, 6-24 carbon atoms; glycidyl(meth)acrylate; an isocyanurate group-containing epoxy compounds, an epoxydized polybutadiene; hydantoin-epoxy resins; epoxy resins obtained by epoxydation of aliphatic and/or cycloaliphatic alkenes, 5 such as dipentene dioxide, dicyclopentadiene dioxide, and vinyl cyclohexene dioxide, and glycidyl groups-containing resins such as polyesters or polyurethanes containing one or more glycidyl groups per molecule, or mixtures of the epoxy resins in question. The epoxy group in these compounds is suitable for reaction with the amino-functional and 10 thiol-functional vinyl ether, acetal, and alkoxy silane compounds.

Examples of at least difunctional isocyanate compounds suitable for use in the adduct in question include aliphatic, cycloaliphatic or aromatic di-, tri- or tetraisocyanates which may be ethylenically unsaturated or not, such as:

- 15 1,2-propylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, hexamethylene diisocyanate, octa-methylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, 2,4,4-trimethyl hexamethylene diisocyanate, dodecamethylene diisocyanate, ω,ω' -dipropyl ether diisocyanate, 1,3-cyclopentane diisocyanate, 1,2-
- 20 cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 4-methyl-1,3-diisocyanato-cyclohexane, trans-vinylidene diisocyanate, dicyclohexyl-methane-4,4'-diisocyanate, 3,3'-dimethyl-dicyclohexyl-methane-4,4'-diisocyanate, a toluene diisocyanate, 1,3-bis(isocyanatomethyl)benzene, a xylene diisocyanate, 1,5-dimethyl-2,4-
- 25 bis(isocyanatomethyl)benzene, 1,5-dimethyl-2,4-bis(2-isocyanatoethyl)-benzene, 1,3,5-tri-ethyl-2,4-bis(isocyanatomethyl)-benzene, 4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 3,3'-diphenyl-4,4'-diisocyanatodiphenyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 4,4'-diisocyanatodiphenyl methane, 3,3'-dimethyl-4,4'-diisocyanatodiphenyl

methane, a diisocyanatonaphthalene, the adduct of 2 molecules of a diisocyanate, e.g., hexamethylene diisocyanate or isophorone diisocyanate, to a diol such as ethylene glycol, the adduct of 3 molecules of hexamethylene diisocyanate to 1 molecule of water (available under the
5 trademark Desmodur N ex Bayer), the adduct of 1 molecule of trimethylol propane to 3 molecules of toluene diisocyanate (available under the trademark Desmodur L ex Bayer), the adduct of 1 molecule of trimethylol propane to 3 molecules of isophorone diisocyanate, compounds such as 1,3,5-triisocyanatobenzene and 2,4,6-triisocyanatotoluene, and the adduct
10 of 1 molecule of pentaerythritol to 4 molecules of toluene diisocyanate. Preferably, an aliphatic or cycloaliphatic di- or triisocyanate having 8-36 carbon atoms is employed.
The isocyanate-functional compounds are suitable for reaction with the amino-functional, thiol-functional, and hydroxyl-functional vinyl ether,
15 acetal, and alkoxy silane compounds.

As suitable di-, tri-, or polyvalent hydroxyl compounds may be mentioned ethylene glycol, propylene glycol, diethylene glycol, tetramethylene diol, neopentyl glycol, hexamethylene diol, cyclohexane diol, bis-(4-hydroxy-
20 cyclohexyl)methane, glycerol, trimethylol ethane, trimethylol propane, tris(2-hydroxyethyl)isocyanurate, and pentaerythritol. Polyols and other suitable hydroxyl-functional compounds such as polyester diols and polyols and polyether diols and polyols have been described, int. al., in H. Wagner and H.F. Sarx, *Lackkunstharze*, 5th edition, 1971 (Carl Hanser Verlag,
25 München).

The polyols are suitable for reaction with isocyanate-functional vinyl ether, acetal, and alkoxy silane compounds.

Suitable ester compounds are esters of polycarboxylic acids and low-boiling alcohols. Examples are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, and tert-butyl esters of di-, tri- or tetracarboxylic acids, such as malonic acid, adipic acid, dimeric fatty acids, maleic acid, fumaric acid,

5 cyclohexane-1,2-dicarboxylic acid, phthalic acid, isophthalic acid, cyclohexane-1,3-dicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, thiophene-1,5-dicarboxylic acid, trimellitic acid, ethylene tetracarboxylic acid, acetylene dicarboxylic acid, and propane-1,1,2,3-tetracarboxylic acid.

These compounds can enter into a reaction with hydroxy-functional and

10 amino-functional vinyl ether, acetal or alkoxy silane compounds.

The compounds with an ethylenically or ethynically unsaturated group can be distinguished into compounds having electron-rich groups and compounds having electron-poor groups. The electron-rich groups can be

15 divided up into two categories: those capable of reacting with hydroxyl-, amino-, and silylhydride-functional vinyl ether, acetal, or alkoxy silane compounds, and those capable of reacting only with silylhydride-functional vinyl ether, acetal or alkoxy silane compounds. Examples of electron-rich alkene or alkyn compounds reactive with hydroxyl, amino or silylhydride

20 groups are: divinyl ethers, vinyl esters of polycarboxylic acids, polyenamines, poly(-1-alkenesulphides), dialkyn ethers, dialkyn thioethers, alkyn esters of polycarboxylic acids.

Examples of electron-rich alkene or alkyn compounds also capable of reacting with silylhydride-functional compounds are: unsaturated fatty acids

25 and their esters or amides, other unsaturated carboxylic acids, except for α,β -unsaturated carboxylic acids, and their esters or amides.

Examples of compounds having electron-poor ethylenic or ethynenic groups are α,β -unsaturated esters, amides, ketones, and other Michael acceptors known from the literature (such as described, e.g., in J. March,

Advanced Organic Chemistry, Reaction, Mechanism and Structure, 4th Ed.
(Wiley Interscience: 1992), p. 795 and the references cited therein).

Representative examples of compounds having at least 2 acryloyl or
5 methacryloyl groups include the (meth)acrylic esters of di-, tri- or polyvalent
polyols, including polyester polyols and polyether polyols; adducts of, on
the one hand, a hydroxyl group-containing (meth)acrylic ester of a polyol to,
on the other, an at least difunctional isocyanate compound; and adducts of
(meth)acrylic acid to an at least difunctional epoxy compound.

10 The acryloyl- and methacryloyl-functional compounds are suitable for
reaction with amine-functional or thiol-functional vinyl ether, acetal or
alkoxysilane compounds.

According to the invention, preference is given to a coating composition in
15 which the vinyl ether, acetal and/or alkoxysilane compounds are covalently
bonded to the alkyd resin by addition via a reactive group such as an
amino, hydroxyl, thiol, hydride, epoxy and/or isocyanate group. To this end
these compounds have to possess at least one group capable of forming
an adduct with the reactive groups present in the alkyd resin.

20 To incorporate vinyl ether groups into the alkyd resin use is made of a
vinyloxyalkyl compound the alkyl group of which is substituted with a
reactive group, such as a hydroxyl, amino, epoxy or isocyanate group,
which is capable of forming an adduct with one or more reactive groups
25 present in the alkyd resin.

Examples of vinyl ether compounds capable of being covalently bonded to
the alkyd resin by addition are ethylene glycol monovinyl ether, butane diol
monovinyl ether, hexane diol monovinyl ether, triethylene glycol monovinyl
ether, cyclohexane dimethanol monovinyl ether, 2-ethylhexane diol

monovinyl ether, polytetrahydrofuran monovinyl ether, tetraethylene glycol monovinyl ether, trimethylol propane divinyl ether, and aminopropyl vinyl ether.

Adducts can be formed, e.g., by reacting the vinyl ether compound

5 containing a hydroxyl group or amino group with an excess of a diisocyanate, followed by the reaction of this free isocyanate groups-containing adduct with the free hydroxyl groups of the alkyd resin. Preferably, a process is employed in which first the free hydroxyl groups of the alkyd resin are reacted with an excess of a polyisocyanate, after which

10 the free isocyanate groups are reacted with an amino group- or hydroxyl group-containing vinyl ether compound. Instead of a diisocyanate, a diester may be employed. Transesterification of the hydroxyl groups present in the alkyd resin with an excess of ester groups of the diester, followed by transesterification or transamidation of the remaining ester groups with

15 hydroxyl-functional vinyl ether compounds and amino-functional vinyl ether compounds, respectively, results in vinyl ether-functional alkyd resins.

Instead of using the process discussed above in which an adduct is formed by reacting isocyanate groups or ester groups with hydroxyl groups or amino groups, it is possible to incorporate (meth)acrylate groups into the

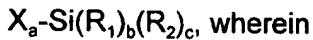
20 alkyd resin during its preparation by carrying out the alkyd resin preparation in the presence of a hydroxy-functional (meth)acrylate ester, such as hydroxyethyl methacrylate (HEMA), and then converting the thus functionalised alkyd resin by means of a Michael reaction with a compound containing a vinyl ether group and a primary amino group, followed by

25 reaction with, e.g., an isocyanate compound in order to obtain a non-basic nitrogen atom.

For the preparation of acetal-functionalised alkyd resins generally use is made of a dialkyl acetal functionalised with an amino group. Examples of

suitable acetal compounds are 4-aminobutyraldehyde dimethyl acetal and 4-aminobutyraldehyde diethyl acetal. The alkyd resin is modified by adding the aminoacetal monomer to an alkyd resin functionalised with isocyanate groups, ester groups of a low-boiling alcohol, or (meth)acrylate groups. The 5 thus obtained dialkyl acetal-modified alkyd resin can be incorporated into a coating composition having a high solids content and a low viscosity. Alternatively, the preparation of acetal-functionalised alkyd resins can take the form of reacting a hydroxyacetal with the carboxyl groups of the alkyd resin or by reacting a diisocyanate or diester compound with the hydroxyl 10 groups of the alkyd resin.

For the incorporation of alkoxy silane groups into the alkyd resin use is made of a siloxane compound having one or more reactive groups which are subsequently reacted with one or more of the constituents making up 15 the alkyd resin. In this process favourable results have been achieved using an alkoxy silane satisfying the formula:



R₁ has the meaning of an alkoxy or oxyalkylene alkoxy group or, if X stands for a hydrogen atom, of a halogen atom, R₂ has the meaning of an 20 aliphatic, cycloaliphatic or aromatic group, and X stands for a hydrogen atom or an alkyl group substituted with an amino, isocyanate, mercapto or epoxy group, wherein a = 1 through 3, b = 1 through 3, c = 0 through 2, and a + b + c = 4.

R₁ preferably is a lower alkoxy group having 1 to 4 carbon atoms in the 25 alkoxy group and R₂ preferably is a group having not more than 18 carbon atoms.

Examples of suitable siloxane compounds are 3-aminopropyl-triethoxysilane, polyglycol ether-modified aminosilane, 3-aminopropyl-trimethoxysilane, 3-aminopropyltris-methoxy-ethoxyethoxysilane, 3-

aminopropyl-methyl-diethoxy silane, N-2-aminoethyl-3-aminopropyl-trimethoxy-silane, N-2-aminoethyl-3-aminopropyl-methyldimethoxy-silane, N-methyl-3-aminopropyl-trimethoxysilane, 3-ureidopropyl-triethoxysilane, 3,4,5-dihydroimidazol-1-yl-propyltriethoxysilane, 3-methacryloxypropyl-trimethoxysilane, 3-glycidyloxypropyl-trimethoxysilane, 3-mercaptopropyl-trimethoxysilane, and 3-mercaptopropyl-methyl-dimethoxysilane, triethoxysilane, diethoxymethyl silane, dimethoxymethyl silane, trimethoxysilane, trichlorosilane, triiodosilane, tribromosilane, dichloromethyl silane, and dibromomethyl silane.

10 The alkyd resin can be modified, e.g., by adding an amino group-modified alkoxy silane to an alkyd resin functionalised with a polyisocyanate or a polyester of a low-boiling alcohol. Hydride-functional alkoxy silanes can be bonded to the alkyd directly, i.e., without modification with a coupling molecule such as a diisocyanate or diester, by adding a compound

15 containing a silylhydride group to an ethylenically unsaturated group in the alkyd resin. This addition is catalysed by a transition metal. In this process it is preferred to make use of a halogenated silylhydride and, on conclusion of the addition reaction, convert it into an alkoxy silane compound with a low-boiling alcohol. The addition reaction proceeds most favourably in the

20 absence of sterically hindering groups and is optimal when the ethylenically unsaturated groups are terminal groups, as is the case with esters of 10-undecenecarboxylic acid. The thus obtained alkoxy silane-modified alkyd resin can be incorporated into a coating composition having a high solids content and a low viscosity.

25 According to the invention, preference is given to a coating composition in which the ratio of the number of oxidatively drying groups present in the alkyd resin to the number of groups reactive in the presence of an acid is in the range of 1/10 to 15/1, with preference being given to a ratio in the

range of 1/3 to 5/1. Instead of a single modified alkyd resin several alkyd resins may be employed, with one alkyd resin being highly modified and the others being less so or not at all. All that is of importance is the ratio of the number of oxidatively drying groups to the number groups reactive in
5 the presence of an acid.

The pKa value of the acid under the influence of which the acid-reactive compounds are activated is < 5, preferably ≤ 3.

Examples of suitable acids are sulphonic acid derivatives, such as methane
10 sulphonic acid, p-toluene sulphonic acid, dodecyl benzene sulphonic acid, phosphoric acid derivatives such as phosphoric acid dibutyl ester and/or suitable substituted carboxylic acid derivatives such as trichloroacetic acid and trifluoroacetic acid. Up to now, optimum results have been obtained using phosphoric acid dibutyl ester.

15 The photo-initiators suitable for use according to the invention generally are compounds activated by low UV-intensities and daylight. Suitable photo-initiators are acyl phosphine oxides, thioxanthone compounds, and mixtures thereof. Both monoacylphosphine oxide photo-initiators, such as
20 are disclosed, for example, in EP-A-0 007 508 and EP-0 413 657, and bisacylphosphine oxide photo-initiators, such as are disclosed, for example, in EP-A-0 184 095, EP-A-0 413 657, GB 2,259,704, and GB 2,292,740, can be used as photo-initiators in the coating composition of the present invention. An example of a monoacylphosphine oxide photo-initiator is
25 (2,4,6-trimethylbenzoyl)-diphenyl-phosphine oxide (Lucirin® TPO). Examples of bisacylphosphine oxide photo-initiators include bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide, bis(2,6-dimethoxybenzoyl)-2,2,4-trimethylpentyl-phosphine oxide, and bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine oxide. Examples of thioxanthone

compounds include 2-isopropyl-thioxanthone, 1-chloro-4-propoxythioxanthone, 2,4-diethoxy thioxanthone, and 2-chlorothioxanthone. Very favourable results have been obtained up to now using bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphine oxide as
5 photoinitiator.

In general, favourable results are obtained when the photo-initiator is present in an amount of 0,01 to 5 wt.%, calculated on the overall amount of ethylenically unsaturated alkyd resin present. In this case preference is
10 given to an amount in the range of 0,01 to 2 wt.%, more particularly, in the range of 0,05 to 2 wt.%. When a sensitiser is employed, preference is given to an amount making up 10 to 200 wt.% of the photo-initiator.

While the ethylenically unsaturated alkyd resin is cured by oxidative drying
15 under the influence of a photo-initiator, the vinyl ethers, acetals and/or alkoxysilanes are cured under the influence of an acid and, in the case of acetals and/or alkoxysilanes, also in the presence of a small amount of moisture from the air. Thus, in order to enhance the storage stability of the coating compositions according to the invention, advantageous use is
20 made of a photo-initiator which releases an acid under the influence of electromagnetic radiation. Such photo-initiators have been disclosed, int. al., by G. Li Bassi et al. in "Photoinitiators for the simultaneous generation of free radicals and acid hardening catalysts," in a paper distributed during a symposium of Chemspec Europe 87 BACS.
25 As an example may be mentioned the compound (MDTA), 2-methyl-1-[4-(methylthiophenyl]-2-[4-methylphenylsulphonyl]propan-1-one, which is commercialised by Fratelli Lamberti Spa, Varese, Italy.

Other latent acids are disclosed, for example, in EP-A-0 139 609, EP-A-0 164 314, EP-A-0 199 672, EP-A-0 571 330, EP-A-0 780 729, and GB 2,306,958.

Alternatively, use may be made of latent acids which are unblocked with
5 moisture from the air. As an example may be mentioned the silyl esters of sulphonic acids, such as trimethylsilyl p-toluene sulphonic acid.

Generally, a small amount of organic solvents is incorporated into the coating compositions according to the invention. Preference is given in that
10 case to solvents which have a flashpoint of at least 55°C and a boiling point in the range of 140°C to 260°C. As an example may be mentioned aliphatic, cycloaliphatic or aromatic hydrocarbons having on average 9-16 carbon atoms per molecule, alcohol ethers, and alcohol ether acetates or mixtures thereof. Examples of such solvents include the hydrocarbon
15 solvents available under the trademarks Shellsol H, Shellsol K, and Shellsol AB, all ex Shell Chemicals, and Solvesso-150 ex Esso, as well as compounds such as ethyl diglycol, ethyl glycol acetate, butyl glycol, butyl glycol acetate, butyl diglycol, butyl diglycol acetate, and methoxypropylene glycol acetate. Preferably, the solvent has a boiling point in the range of
20 170°C to 230°C. If so desired, small amounts of ethers, esters, ketones, alcohol esters, and alcohols and glycols may be present in the coating composition.

If so desired, the coating composition according to the invention may
25 contain all sorts of additives or adjuvants, e.g., pigments, dyes, fillers, anti-oxidants, anti-ozonants, gloss-reducing agents, thixotropic agents, sterically hindered amines, bactericides, fungicides, anti-skinning agents, perfumes, anti-foaming agents, drying stabilisers, finely dispersed waxes

and polymers such as hydrocarbon resins, colophonium resins, phenol resins, and ketone resins.

Suitable pigments are, e.g., natural or synthetic pigments which may be

5 transparent or not. Examples of suitable pigments are titanium dioxide, red iron oxide, orange iron oxide, yellow iron oxide, phthalocyanine blue, phthalocyanine green, molybdate red, chromium titanate, and earth colours such as ochres, green earths, umbers, and burnt or raw Siennas. In general, pigments for finishes are used in an amount of not more than 150

10 wt.%, preferably 50-125 wt.%, vis-à-vis the alkyd resin (calculated as dry solid). Examples of suitable thixotropic agents are inorganic agents such as organically modified magnesium montmorillonites, e.g., those available under the trademarks Bentone 27 and 38 ex National Lead Co., but preferably adducts of a diisocyanate, say, hexamethylene diisocyanate, to

15 a monoamine or hydroxy-monoamine having 1 to 5 aliphatic carbon atoms, e.g., benzyl amine, adducts of a symmetric aliphatic or homocyclic diisocyanate to a mono- or diamine having at least a primary amino group and an ether group, and adducts of an isocyanurate-trimer of a diisocyanate having 3-20 carbon atoms to an amine having one or more

20 primary amino groups.

The coating compositions can be applied to a substrate in any suitable manner, e.g., by means of roller coating, spraying, brushing, sprinkling, flow coating or dipping. Preferably, the composition is applied by brushing.

25

Suitable substrates include metals or synthetic materials, wood, concrete, cement, brick, paper or leather, all of which may have been pre-treated or not. Suitable metals include iron, steel, and aluminium. The applied coat can be cured very suitably at a temperature of, e.g., 0-40°C. Optionally, a

curing temperature above 40°C may be employed, as a result of which the curing time can be reduced.

The invention will be further illustrated with reference to the following examples. Needless to say, these are exemplified embodiments to which the invention is not limited.

Unless otherwise specified, "parts" stands for "parts by weight" and "%" for "per cent by weight" in what follows. The solids content SC was calculated or determined in accordance with ISO 3251-1993 after one hour of heating at 120°C and is given in wt.%. The viscosity was determined at 23°C using a viscosimeter as specified by Brookfield (spindle 4 and motor set at 30) and is given in cPa.s. The acid value and the hydroxyl number value are given in mg KOH per gram of resin. The molecular weights were determined by means of GPC (THF as mobile phase and polystyrene as standard). The coating compositions to be tested each had a viscosity of ± 40 cPa.s (Cone and Plate, 10 000 s⁻¹) as a result of dilution with butyl acetate. They were cured with the aid of a BK drying recorder originating from The Mickle Lab. England Co., Gomshall, Surrey, England.

The results obtained in this fashion can be classified as follows:

- 20 Phase 1 : the line traced by the pin closes up again.
- Phase 2 : the pin traces a scratchy line ("dust free").
- Phase 3 : the pin traces a straight line in the paint which does not close up again.
- Phase 4 : the pin leaves no further trace ("hardened through").
- 25 The outcome is indicated per phase through the number of hours during which the pin shows the effect for that particular phase. The more hours listed for a particular phase, the slower the curing process will proceed during that phase.

The strength of the film was determined with a fingernail on films applied to a sheet of glass in such a thickness as to give a dry film of 40 - 50 µm. In this process the nail is put at right angles to the film and moved slightly.

The results of this test are represented as follows:

- 5 -- = Film damaged by exerting minimal pressure on substrate
- = Film damaged by exerting slight pressure
- ± = Film damaged by exerting pressure
- + = Film not damaged, but deformed (nail imprint remains visible)
- ++ = Film not damaged (no remaining nail imprint).

10

The abbreviations used in the examples below have the following meanings:

- AMEO-T : 3-aminopropyl triethoxysilane (Mw=222)
- BAPO : bis(2,6-dimethylbenzoyl)-2,4,4-trimethylpentyl phosphine oxide
- 15 DEM : diethyl malonate
- HBVE : 4-hydroxybutyl vinyl ether
- PENTA : pentaerythritol
- MA : maleic anhydride
- IPDI : isophorone diisocyanate
- 20 DBF : phosphoric acid dibutyl ester
- MDTA : 2-methyl-1-[4-(methylthiophenyl]-2-[4-methylphenylsulphonyl] propan-1-one (latent acid ex Fratelli Lamberti Spa, Italy)
- SC : solids content (determined after 60 minutes of drying at 120°C in accordance with ISO 3251- 1993).

25

Example I

1.1 Preparation of hydroxyl-functional alkyd resin

1697 (6,0 moles) parts of ricinenic fatty acid (commercially available as Nouracid DE554 ex Akzo Nobel Chemicals), 409 g (3,0 moles) of PENTA,

and 2,1 g of maleic acid were mixed and heated, with constant stirring, to 185°C over 50 minutes. At 240°C xylene was added, and the water of reaction was removed, with refluxing, until an acid value of 1,7 was achieved. After cooling an alkyd resin having the following properties was 5 obtained, the values listed being related to a solids content of 100%.

Solids content SC (theory)	100
Acid value mg KOH/g	1,7
Hydroxyl number (theory) mg KOH/g	169
Number average molecular weight Mn	1323
Weight average molecular weight Mw	1661

1.2 Preparation of alkoxy silane-functional alkyd resin (alkyd resin A)

560 g (1,69 hydroxyl equivalent) of the alkyd resin prepared above were mixed with 263 g (1,64 moles) of DEM in 17,5 g of xylene, after which the 10 mixture was heated to 197°C and kept for 80 minutes at said temperature with refluxing. After removal of the ethanol the temperature was lowered to 122°C and 381 g (1,72 moles) of AMEO-T were added, followed by an increase in the temperature to 200°C and distilling off of ethanol. When, after 30 minutes, no further ethanol came over, the pressure was lowered 15 to 600 mbar. Next, another 85 g of ethanol was distilled off. After removal of the xylene from the reaction mixture there was obtained an alkoxy silane-functional alkyd resin having the following properties:

Solids content SC (theory)	100
Acid value mg KOH/g	0,8
Number average molecular weight Mn	1774
Weight average molecular weight Mw	3905
Viscosity in cPa.s	49

Example II2.1 Preparation of hydroxyl-functional alkyd resin

In a three-necked flask equipped with a stirrer and a distillation column a mixture composed of 1275 g (4,5 moles) of ricinenic fatty acid
5 (commercially available as Nouracid DE554 ex Akzo Nobel Chemicals), 246 g (1,8 moles) of PENTA, and 1,5 g of MA was heated to 186°C, with the water released during the reaction being distilled off. Next, 188 g of xylene were added, and the reaction mixture was heated at 240°C, with refluxing, until no further water came over. After cooling with nitrogen the
10 reaction mixture was left to stand overnight, after which the xylene was distilled off *in vacuo* at a temperature < 200°C. The intermediate product had the following properties:

Solids content SC (theory)	100
Acid value mg KOH/g	1,0
Number average molecular weight Mn	1378
Weight average molecular weight Mw	1745
Viscosity, cPa.s	25
OH-number (theory)	105

2.2 Preparation of alkoxy silane-functional alkyd resin (alkyd resin B)

15 Charged into a 2000 ml three-necked flask equipped with a stirrer and a distillation column was a mixture composed of 154 g of methoxypropyl acetate, 294 g (2,64 eq. NCO) of IPDI, and 0,3 g of dibutyl tin dilaurate, after which the temperature was raised to 80°C. To this mixture were added, over a period of 2 hours, 705 g (1,32 eq. hydroxyl) of the hydroxyl-
20 functional alkyd resin prepared as specified in 2.1. On conclusion of the dosing a further 35 g of methoxypropyl acetate were added, and the reaction mixture was stirred at about 80°C until the content of free isocyanate was 4,68%, based on the solution. The reaction mixture was

then cooled to 25 to 30°C, and over a period of 1 hour 280 g (1,27 moles) of AMEO-T were added, with care being taken to ensure that the temperature did not rise above 40°C. After cooling 321 g of methoxypropyl acetate were added. When the free isocyanate content was no longer

5 subject to change, 44 g of n-butanol were added. The thus obtained product had the following properties:

Acid value mg KOH/g	0,4
Viscosity, cPa.s	65
Number average molecular weight Mn	2088
Weight average molecular weight Mw	3169
Solids content SC (theory)	70,0

Example III

Preparation of acetal-functional alkyd resin (alkyd resin C)

10 250 g (0,75 hydroxyl equivalent) of the alkyd resin prepared as specified in 1.1 were mixed with 114 g (0,72 mole) of DEM in xylene, after which the mixture was heated to 180°C and kept at that temperature with refluxing.

After removal of the ethanol the temperature was lowered to 100°C, and 93,8 g (0,71 mole) of 4-aminobutyraldehyde dimethyl acetal were added,

15 followed by an increase in the temperature to 180°C and distilling off of ethanol. The remaining ethanol was then removed under reduced pressure. Obtained was an acetal-functional alkyd resin having the following properties:

Solids content SC (theory)	100
Amine number mg KOH/g	0,5
Number average molecular weight Mn	1421
Weight average molecular weight Mw	5280
Viscosity in cPa.s	902

Example IVPreparation of vinyl ether-functional alkyd resin (alkyd resin D)

A mixture of 141 g (0,55 mole) of dipentaerythritol and 614 g (2,2 moles) of ricinenic fatty acid (commercially available as Nouracid DE554 ex Akzo Nobel Chemicals) was mixed and heated to 240°C, after which xylene was added and the water of reaction was removed, with refluxing, until an acid value < 2 was achieved. Following cooling to 160°C the xylene was removed under reduced pressure. Next, 178 g (1,1 moles) of DEM and 129 g (1,1 moles) of HBVE were added. The transesterification reaction started at 155°C, with formed ethanol being distilled off. After removal of the remaining ethanol at 155°C and 15 mBar a product having the following properties was obtained:

Solids content SC (theory)	100
% free HBVE (determined by liquid chromatography, HPLC)	<0,1%
Number average molecular weight Mn	2284
Weight average molecular weight Mw	7731
Viscosity in cPa.s	100

Examples V and VI and Comparative Example A (without acid)

15 50,3 parts of alkyd resin A of Example I were mixed with 50 parts of a commercially available alkyd resin (Setal 294-SK94 ex Akzo Nobel Resins) with a high solids content and the following composition:

Acid value	14
Hydroxyl number	40
Viscosity, Pa.s	4,5
Number average molecular weight Mn	1600-2000
Oil length	85
Solids content SC	94

and 5,2 parts of a 10% solution of the photo-initiator BAPO in butanol, 0, 2,6, and 5 parts, respectively, of a 10% solution of DBF in butyl acetate, 5, 2,5, and 1,5 parts, respectively, of n-butanol, as well as 5, 2,5, and 1,5 parts, respectively, of methoxypropyl acetate.

- 5 The composition of the tested compositions (in parts by weight), the drying results, and the film properties of the topcoats applied with the compositions are listed in Table 1.

Table 1

Example	A (comparison)	V	VI
Alkyd resin A	50,3	50,3	50,3
Setal 294-SK94	50	50	50
10 wt.% sol. DBF	0	2,6	5
10 wt.% sol. BAPO	5,2	5,2	5,2
n-butanol	5	2,5	1,5
methoxypropyl acetate	5	2,5	1,5
BK recorder Phase 1	2,75	1,75	1
Phase 2	3,75	2,5	1,5
Phase 3	9,5	7,25	3,25
Phase 4	21	9	3,25
film strength after 1 week	±	±	±

- 10 The results listed in Table 1 clearly show that the curing of alkyd resin A (in the absence of an acid) proceeds too slowly for it to be used successfully in house paints, this despite the fact that the final film strength of all topcoats after 1 week was sufficient.
- 15 Examples VII to XII and Comparative Examples B to I
Alkyd resin B was tested in an analogous manner in combination with Setal 294-SK94.
Comparative example B shows the drying time for a Setal 294-SK94-containing composition into which, unlike in the case of the compositions according to the invention, groups which react in the presence of an acid

have not been incorporated, but a cobalt siccative for the oxidatively drying alkyd resin has. Comparative examples D to F show the result of the combined use of a metal siccative and an acid in the curing of groups which are cured under the influence of an acid. Comparative examples C, 5 G, H, and I clearly show that without the acid required to activate the groups reacting in the presence of an acid, curing after 24 hours in particular is unsatisfactory. The composition of the coating compositions and the results of the drying tests performed are listed in Table 2.

10

Table 2

Example	B	C	D	E	F	G	VII
Alkyd resin B		68,1	68,1	68,1	68,1	68,1	68,1
Setal 294-SK94	100	50	50	50	50	50	50
Cobalt salt	0,6	0,6	0,6	0,6	0,6		
methyl ethyl ketoxime	0,54	0,54	0,54	0,54	0,54		
white spirit		7,3	7,3	7,3	7,3	7,3	7,3
10% sol. DBF			1,4	2,5	10,6		2,5
BAPO						0,1	0,1
BK recorder Phase 1	2	2	3	0,75	0,25	2	0,5
Phase 2	2,75	2,25	4	2,75	0,25	3	0,75
Phase 3	3,25	2,5	7,25	9,5	0,75	> 18	2
Phase 4	3,5	3,25	14,5	13,75	1,5		2,5
film strength after 1 day	+	+	+	±	--	-	-
film strength after 1 week	+	+	+	+	+	+	+

Example	VIII	H	IX	X	I	XI	XII
Alkyd resin B	68,1	68,1	68,1	68,1	68,1	68,1	68,1
Setal 294-SK94	50	50	50	50	50	50	50
white spirit	7,3	7,0	4,0	2,0	7,3	7,3	7,3
10% sol. DBF	5		2,5	5		2,5	5
BAPO	0,1	0,5	0,5	0,5	1,0	1,0	1,0
BK recorder Phase 1	< 0,25	1,5	0,5	0,25	1,25	0,25	0,25
Phase 2	0,25	2,25	0,75	0,25	1,75	0,5	0,25
Phase 3	1	> 18	1,75	1	11,5	1	1
Phase 4	2,25		2,25	1	16,25	1,75	1
film strength after 1 day	-	-	±	±	±	±	±
film strength after 1 week	+	+	+	+	+	+	+

The results listed in Table 2 clearly show that the most rapid curing is achieved when use is made of a binder composition based on an 5 oxidatively drying alkyd resin having acid reactive groups in combination with an acid and a radical initiator.

Examples XIII and XIV and Comparative Examples J-M

The acetal-functional alkyd resin C was mixed with an equal amount by 10 weight of Setal 294-SK94. The initiator/catalyst used was a 10% solution of the photo-initiator BAPO in butanol, in combination or not with the latent acid MDTA, with dodecyl benzene sulphonic acid (DDBSA), or just with DDBSA, BAPO, or a standard drier combination based on a cobalt siccative (0,06 wt.% Co based on the solid constituents) and a six-fold 15 equimolar excess of the anti-skinning agent methylethyl ketoxime.

The evaluation was carried out in a conditioned room (23°C, 55% RH). For lighting use was made of fluorescent light (TL055 ex Philips). The composition of the coating compositions and the results of the drying tests performed are listed in Table 3.

Table 3

Example	XIII	XIV	J	K	L	M
Alkyd resin C	50	50	50	50	50	50
Setal 294-SK94	50	50	50	50	50	50
% Co-salt						0,06
% BAPO	0,5	0,5			0,5	
% MDTA	1		1			
% DDBSA		1		1		
BK recorder Phase 1	2,75	0,75	6,5	8,25	2	1,5
Phase 2	5,25	1,75	10,75	> 21	3,25	5,25
Phase 3	> 20	9,25	> 20		4	9,75
Phase 4		> 21			6,75	> 21
film strength after 1 day	±	±	--		-	-

The results listed in Table 3 clearly show that the most rapid curing is achieved when use is made of a binder composition based on an oxidatively drying alkyd resin having acid reactive groups in combination with an acid which may be blocked or not and a radical initiator.

Example XV and Comparative Example N-O

In a manner analogous to that indicated in Example XIII, the vinyl ether-functional alkyd resin D was mixed with an equal amount by weight of Setal 294-SK94. The initiator/catalyst used was a 10% solution of the photo-initiator BAPO in butanol, in combination or not with the latent acid MDTA. In addition, for comparative purposes a mixture of alkyd resin D and Setal 294-SK94 was dried in the absence of both initiator and latent acid.

The composition of the coating compositions and the results of the drying tests performed in the presence of fluorescent light (TL055 ex Philips) are listed in Table 4.

Table 4

Example	XV	N	O
Alkyd resin D	50	50	50
Setal 294-SK94	50	50	50
% BAPO	0,5	0,5	
% MDTA	1		
% SC	86,4	86,7	
η (cPa.s) start	40	41	39
η (cPa.s) after 5 weeks	96	74	64
BK recorder Phase 1	1	1,5	> 20
Phase 2	2,25	2,5	
Phase 3	2,5	3	
Phase 4	4,5	> 20	

The results listed in Table 4 clearly show that the most rapid curing is achieved when use is made of a binder composition based on an
5 oxidatively drying alkyd resin having acid reactive groups in combination with a blocked acid and a radical initiator.

The drying tests of Table 4 were repeated, with the proviso that this time they were carried out in the presence of fluorescent light with a higher
10 content of UV-light. In this process use was made of four fluorescent lights of 40 Watt each (TL03 ex Philips, λ_{max} at 420 nm) positioned at a distance of about 20 cm from the object to be cured. The outcome of the measurements is listed in Table 5.

Table 5

Example	XV	O
Alkyd resin D	50	50
Setal 294-SK94	50	50
% BAPO	0,5	0,5
% MDTA	1	
% SC	86,4	86,7
η (cPa.s) start	40	41
η (cPa.s) after 5 weeks	96	74
BK recorder Phase 1	< 0,1	0,5
Phase 2	0,6	1
Phase 3	1,1	1,6
Phase 4	2	3,25

The results listed in Table 5 clearly show that the effect of rapid curing according to the invention is much more manifest in the case of exposure of light using a radiation source with a higher percentage of UV-light. While it is possible to achieve comparatively rapid drying using just BAPO, the film strength finally obtained remains insufficient.

The major increase in viscosity after a residence time of 6 weeks at 50°C can be reduced substantially by lowering the acid value of Setal 294-SK94 from 14 (see Examples V and VI) to less than 1. When 50 parts of such a resin with a lowered acid value (e.g., 0,7) are mixed with 50 parts of the vinyl ether-functional alkyd resin D of Example IV, the viscosity at 50°C after one week will only increase from 32 to 39 cPa.s and after six weeks at 50°C it will only have increased to 45 cPa.s.

Claims

1. A non-aqueous coating composition based on an oxidatively drying alkyd resin and a photo-initiator, characterised in that an acid or latent acid and one or more compounds of the group of vinyl ethers, acetals, and alkoxysilanes which are reactive in the presence of an acid are incorporated into the coating composition.
5
2. A coating composition according to claim 1, characterised in that the vinyl ether, acetal and/or alkoxysilane compounds are covalently bonded to the alkyd resin.
10
3. A coating composition according to claim 2, characterised in that the vinyl ether groups in the alkyd resin are obtained by the incorporation therein of a vinyloxyalkyl compound the alkyl group of which is substituted with a hydroxyl, amino, epoxy or isocyanate group.
15
4. A coating composition according to claim 2, characterised in that the acetal groups in the alkyd resin are obtained by the incorporation therein of a dialkyl acetal functionalised with an amino group.
20
5. A coating composition according to claim 2, characterised in that the alkoxysilane groups in the alkyd resin are obtained by the incorporation therein of an alkoxysilane of the formula
25
$$X_a\text{-Si}(R_1)_b(R_2)_c$$
, wherein
R₁ has the meaning of an alkoxy or oxyalkylene alkoxy group or, if X stands for a hydrogen atom, of a halogen, R₂ has the meaning of an aliphatic, cycloaliphatic or aromatic group, and X stands for a

hydrogen atom or an alkyl group substituted with an amino, isocyanate, mercapto or epoxy group, with $a = 1$ through 3, $b = 1$ through 3, $c = 0$ through 2, and $a + b + c = 4$.

- 5 6. A coating composition according to claim 1, characterised in that the ratio of the number of oxidatively drying groups present in the alkyd resin to the number of groups reactive in the presence of an acid is in the range of 1/10 to 15/1.
- 10 7. A coating composition according to claim 6, characterised in that the ratio of the number of oxidatively drying groups present in the alkyd resin to the number of groups reactive in the presence of an acid is in the range of 1/3 to 5/1.
- 15 8. A coating composition according to claim 1, characterised in that the acid has a pKa value < 5.
9. A coating composition according to claim 8, characterised in that the acid has a pKa value ≤ 3 .
- 20 10. A coating composition according to claim 1, characterised in that the acid is a compound selected from the group of sulphonic acid derivatives, such as methane sulphonic acid, p-toluene sulphonic acid, dodecyl benzene sulphonic acid, phosphoric acid derivatives such as phosphoric acid dibutyl ester and/or suitable substituted carboxylic acid derivatives such as trichloroacetic acid and trifluoroacetic acid.
- 25

11. A coating composition according to claim 10, characterised in that the acid is the phosphoric acid dibutyl ester.
12. A coating composition according to claim 1, characterised in that the acid present in the latent acid is released by a photo-induced reaction.
5
13. A coating composition according to claim 1, characterised in that the acid present in the latent acid is released by hydrolysis.
10
14. Alkyd resin having substantially no unsaturated groups in the backbone and comprising vinyl ether groups.
15. A process for the preparation of an alkyd resin according to claim
15 14, characterised in that the vinyl ether groups in the alkyd resin are obtained by the incorporation therein of a vinyloxyalkyl compound the alkyl group of which is substituted with a hydroxyl, amino, epoxy or isocyanate group.

INTERNATIONAL SEARCH REPORT

Intern	Application No
PCT/EP 99/01136	

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D167/08 C08G63/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 009 356 A (IMPERIAL CHEMICAL INDUSTRIES) 2 April 1980 see page 2, line 3 - line 18; claims 1-12	1,6-10
A	US 3 825 428 A (DAVIDSON) 23 July 1974 see claims 1-5	1-3,5
A	GB 1 423 408 A (VIANOVA KUNSTHARZ AG) 4 February 1976 see claims 1-11	1-3,5
A	US 3 373 160 A (IKEDA) 12 March 1968 see column 4, line 22 - line 38; claim 1	1,3,4
A	US 5 286 835 A (GREEN ET AL.) 15 February 1994 see claims 1,10	14,15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/EP 99/01136

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 9356	A 02-04-1980	AT 5081 T AU 5078379 A CA 1136337 A DK 405379 A GB 2031918 A,B JP 1375967 C JP 55045797 A JP 61039988 B NZ 191553 A US 4294887 A ZA 7904811 A ZW 18079 A		15-11-1983 03-04-1980 23-11-1982 28-03-1980 30-04-1980 22-04-1987 31-03-1980 06-09-1986 16-03-1981 13-10-1981 24-09-1980 06-05-1981
US 3825428	A 23-07-1974	NONE		
GB 1423408	A 04-02-1976	AT 319428 B AT 313439 B CH 594004 A DE 2313098 A FR 2192154 A SE 400572 B CH 580650 A DE 2313111 A FR 2192155 A GB 1422872 A		15-03-1974 15-01-1974 30-12-1977 31-01-1974 08-02-1974 03-04-1974 15-10-1976 24-01-1974 08-02-1974 28-01-1976
US 3373160	A 12-03-1968	NONE		
US 5286835	A 15-02-1994	AT 172995 T CA 2142269 A DE 69321961 D DE 69321961 T EP 0656028 A JP 2744849 B JP 7506620 T WO 9404594 A		15-11-1998 03-03-1994 10-12-1998 12-05-1999 07-06-1995 28-04-1998 20-07-1995 03-03-1994